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Chlorobis(1,10-phenanthroline)copper(II) chloride methanol solvate 4.5-hydrate

Liping Lu, Shidong Qin, Pin Yang and Miaoli Zhu*

Institute of Molecular Science, Chemical Biology and Molecular Engineering Laboratory of Education Ministry, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China

Correspondence e-mail: miaoli@sxu.edu.cn

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Key indicators

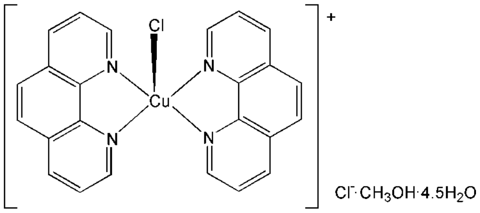
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.011 Å
R factor = 0.097
wR factor = 0.279
Data-to-parameter ratio = 13.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $[CuCl(C_{12}H_8N_2)_2]Cl\cdot CH_3OH\cdot 4.5H_2O$, the coordination geometry around the Cu atom is that of a trigonal bipyramid, with the central Cu atom bound to one Cl atom and four N atoms of the two phenanthroline ligands. The dihedral angle between the two phenanthroline planes is 49.6 (1)°; the dihedral angles between these planes and the equatorial plane of the trigonal bipyramid are 79.2 (1) and 88.4 (1)°.

Comment

The copper(I) complex of 1,10-phenanthroline (phen), the first artificial nuclease, has been thoroughly investigated over the past two decades. Recently, it has been used to study the interaction of DNA and proteins (Chen *et al.*, 2001). Although $[(phen)_2Cu]^+$ or $[(phen)Cu]^+$ are supposed to be the active species for DNA cleavage (Sigman *et al.*, 1993; Lu *et al.*, 2003), it is still not known how these complexes bind to DNA. Therefore, investigating the structures of $[(phen)_2Cu]^+$ and $[(phen)Cu]^+$ or $[(phen)_2Cu]^{2+}$ and $[(phen)Cu]^{2+}$ would be helpful in understanding the binding mode. In researching DNA cleavage properties of Cu/phen/L-His, compound (I) was obtained. It differs from other copper complexes with phenanthroline (Dobson *et al.*, 1984; Healy *et al.*, 1985) in having a fifth coordinated atom, *viz*. Cl.



(I)

The geometric parameters of (I) are listed in Table 1 and the molecular structure is illustrated in Fig. 1. In this complex, copper is five-coordinated by four N atoms from two 1,10-phenanthroline ligands and one Cl atom. This is different from $[Cu(H_2O)(phen)_2](NO_3)_2$, (II) (Nakai & Deguchi, 1975), where the fifth coordination site is occupied by a water O atom. The Cu—N bond lengths lie in the range 1.979 (6)–2.105 (6) Å, in good agreement with those in (II). The Cu—Cl bond distance is 2.351 (2) Å, shorter than that in a hydroxo-bridged dinuclear copper–phen complex [Cu—Cl = 2.602 (1) Å; Lu *et al.*, 2003] and in chloro(L-glutamato)(1,10-phenanthroline)copper(II) [Cu—Cl = 2.590 (3) and 2.608 (3) Å; Lu *et al.*, 2004].

As shown in Fig. 1, the cation of (I) has approximate twofold rotation symmetry, the twofold axis lying along the

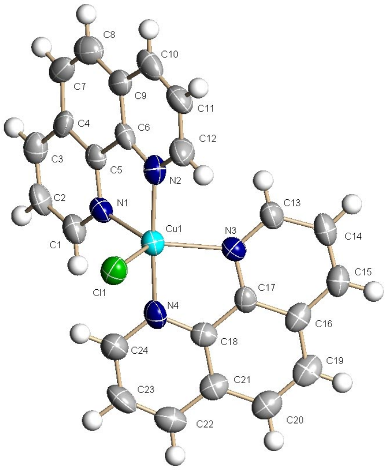


Figure 1
The structure of the cation of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

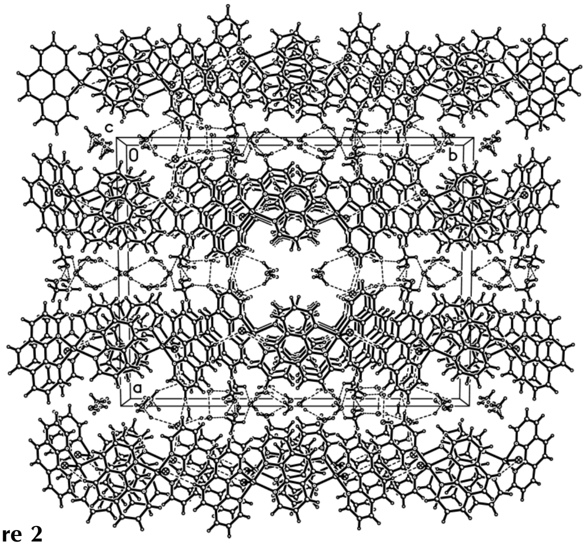


Figure 2
A packing diagram of (I), viewed along the *c* axis. Hydrogen bonds are indicated by dashed lines.

Cu—Cl bond; compound (II) exhibits exact twofold symmetry. The coordination geometry about the Cu atom is that of a distorted trigonal bipyramid. The axial positions are occupied by N2 and N4, while atoms Cu1, N1, N3 and Cl1 lie in the equatorial plane; Cu1 deviates by 0.020 (2) Å from the plane of N1, N3 and Cl1.

The angles N2—Cu1—Cl1 and N4—Cu1—Cl1 are 91.0 (1) and 92.2 (1)°, respectively, larger than that in (II) [85.5 (4)°]. Thus, in (I), the axial Cu—N bonds are almost perpendicular to the equatorial plane. The angles in this plane, *viz*. N1—Cu1—Cl1, N3—Cu1—Cl1 and N3—Cu1—N1, are 115.1 (2), 120.3 (2) and 124.6 (2)°, respectively, somewhat different from the corresponding angles in (II) [110.0 (4), 110.1 (4) and 139.6 (4)°].

The maximum deviation from the phenanthroline plane C1–C12/N1/N2 is 0.037 (1) Å for C2, and that for the plane C13–C24/N3/N4 is 0.022 (7) Å for C15. The dihedral angle between these two phenanthroline planes is 49.6 (1)°, larger than that in (II) (*ca* 40°). The dihedral angles between the two phenanthroline planes and the equatorial plane of the trigonal bipyramid are 79.2 (1) and 88.4 (1)°.

The crystal packing is characterized by intermolecular hydrogen bonds involving anions as well as all O atoms of the solvent water molecules.

Experimental

The chemicals were commercially available (reagent grade) and used without further purification. The title complex was synthesized by preparing a 1:1:1 molar ratio of copper dichloride dihydrate, 1,10-phenanthroline hydrate and L-His in methanol–water (1:1). A microcrystalline solid formed after one week as the solvent slowly evaporated. A sample of suitable dimensions for X-ray single-crystal diffraction was recrystallized from a mixed CH_3OH–H_2O solution (90/10). Analysis (%) found: C 49.29, H 4.76, N 9.47, Cl 11.32; calculated for $C_{25}H_{29}Cl_2CuN_4O_{5.5}$: C 49.39, H 4.81, N 9.32, Cl 11.66. CHN were analysed in a Perkin-Elmer 240 C Elemental Analyzer. Cl^- was titrated with 0.1 *M* $AgNO_3$ solution.

Crystal data

$[CuCl(C_{12}H_8N_2)_2]Cl\cdot CH_4O\cdot 4.5H_2O$
$M_r = 607.96$
Monoclinic, $C2/c$
$a = 23.387 (5)$ Å
$b = 30.418 (7)$ Å
$c = 7.3816 (16)$ Å
$\beta = 97.714 (3)°$
$V = 5204 (2)$ Å^3
$Z = 8$
$D_x = 1.552$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4822 reflections
$\theta = 2.2$–$25.2°$
$\mu = 1.09$ mm^{-1}
$T = 173 (2)$ K
Block, green
0.38 × 0.30 × 0.20 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{\min} = 0.682$, $T_{\max} = 0.811$
12342 measured reflections
4524 independent reflections
3292 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.075$
$\theta_{\max} = 25.0°$
$h = -24 \rightarrow 27$
$k = -36 \rightarrow 36$
$l = -8 \rightarrow 5$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.097$
$wR(F^2) = 0.279$
$S = 1.06$
4524 reflections
343 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1394P)^2 + 34.1552P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.04$ e Å^{-3}
$\Delta\rho_{\min} = -0.80$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.979 (6)	Cu1—N1	2.105 (6)
Cu1—N4	1.986 (7)	Cu1—Cl1	2.351 (2)
Cu1—N3	2.087 (5)		
N2—Cu1—N4	176.1 (2)	N3—Cu1—N1	124.6 (2)
N2—Cu1—N3	95.2 (2)	N2—Cu1—Cl1	91.03 (17)
N4—Cu1—N3	81.3 (2)	N4—Cu1—Cl1	92.15 (18)
N2—Cu1—N1	81.5 (2)	N3—Cu1—Cl1	120.27 (16)
N4—Cu1—N1	99.2 (2)	N1—Cu1—Cl1	115.06 (16)
N2—Cu1—N1—C1	179.5 (6)	Cl1—Cu1—N1—C1	−93.3 (6)
N3—Cu1—N1—C1	89.1 (6)	N2—Cu1—N1—C5	0.8 (4)

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Table 2
Hydrogen-bonding geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$O6W—H6WA\cdots O5W^{i}$	0.84	2.09	2.90 (2)	163
$O5W—H5WB\cdots O4W^{ii}$	0.82	2.36	2.936 (12)	128
$O4W—H4WA\cdots O5W^{iii}$	0.82	2.17	2.936 (12)	156
$O3W—H3WA\cdots Cl2^{iii}$	0.81	2.13	2.847 (17)	148
$O3W—H3WB\cdots O3W^{i}$	0.80	2.41	2.786 (17)	110
$O2W—H2WA\cdots Cl2^{iv}$	0.85	2.75	3.40 (6)	134
$O1W—H1WA\cdots O2W^{v}$	0.85	2.06	2.61 (6)	122

Symmetry codes: (i) $1-x, y, \frac{1}{2}-z$; (ii) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $1-x, 1-y, 1-z$; (v) $x-1, y, z$.

The residual electron density has a maximum located 0.483 Å from atom H25*C*. H atoms attached to C atoms were placed in geometrically idealized positions, with $Csp^2—H$ = 0.95 Å (phenanthroline) and $Csp^3—H$ = 0.98 Å (methanol), and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(Csp^2)$ and $U_{iso}(H) = 1.5U_{eq}(Csp^3)$. The H atom attached to the methanol O atom was placed in a geometrically idealized position, and constrained to ride on its parent atom, with $U_{iso}(H) = 1.5U_{eq}(O)$. H atoms on O atoms of solvent water were located in difference Fourier maps and their overall U_{iso} value was refined. The O—H distances are in the range 0.78–0.85 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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